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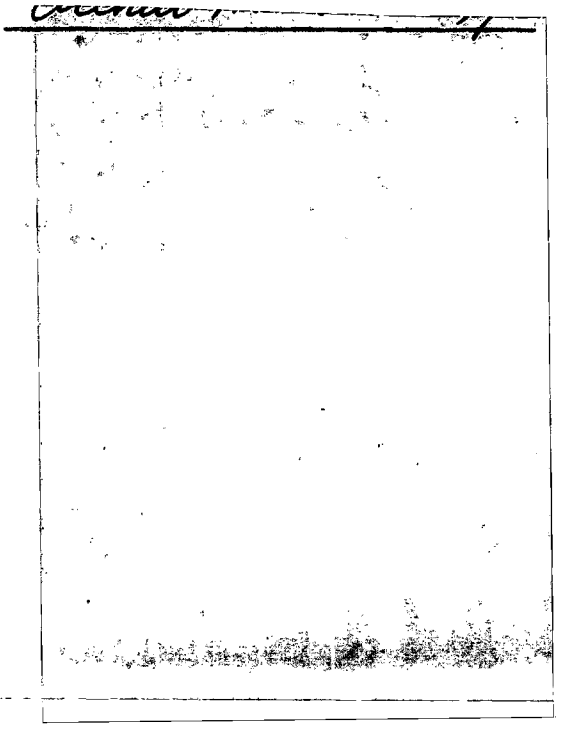

THE MECHANISM OF THE BASIC HYDROLYSIS OF HALOFORMS

A THESIS

Presented to

the Faculty of the Graduate Division

by

Arthur Maultsby Dowell, Jr.

In Partial Fulfillment

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Doctor of Philosophy in Chemistry

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THE MECHANISM OF THE BASIC HYDROLYSIS OF HALOFORMS

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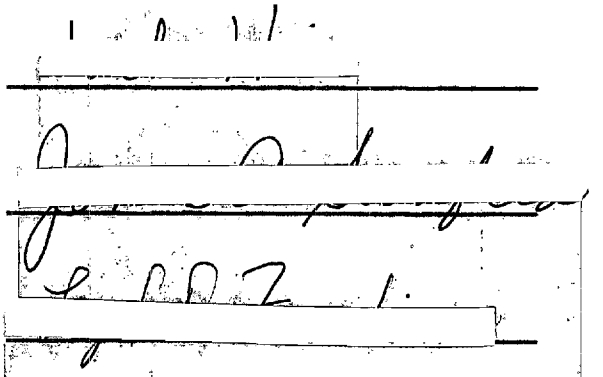

Date approved by Chairman: April 22, 1954

ACKNOWLEDGMENT

I wish to express my appreciation to Dr. Jack Hine for his suggestion of the problem and his valuable aid and guidance during its progress. I also wish to thank the National Science Foundation and the Graduate Division of the Georgia Institute of Technology for granting me fellowships. I wish to thank my wife and children for their patience and encouragement, without which I could never have completed this work.

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SUMMARY

Although it was previously shown that the basic hydrolysis of chloroform probably proceeds by a mechanism involving the trichloromethyl carbanion and carbon dichloride as intermediates, it was not possible to prove conclusively that the reaction does not proceed either by the S_N2 attack of water molecules upon the trichloromethyl anion or by the S_N2 attack of hydroxide ions upon chloroform.

Since the carbon dihalide mechanism involves the loss of a chloride ion from the trichloromethyl anion by an S_N1 reaction in the rate determining step, it was believed that demonstration of a mass law effect would offer conclusive proof of the carbon dihalide mechanism. Accordingly, the rate of basic hydrolysis of chloroform was determined in the presence of several added salts at several concentrations.

Although the effects of sodium fluoride, nitrate, and perchlorate upon the rate of this reaction differed by amounts within the experimental error, the reaction was slowed by identical concentrations of chloride, bromide, and iodide ions. In the case of sodium chloride, this was due to a mass law effect produced by the recombination of carbon dichloride with chloride ions. Combination of carbon dichloride with bromide and iodide ions yielded dichlorobromomethane and dichloroiodomethane, the latter compound having been isolated. In agreement with expectation, the rate constants obtained in the presence of bromide and iodide ions climb with time because the haloforms produced by the reactions of these ions with carbon dichloride are more reactive than

chloroform. Good agreement was found between the magnitude of the decrease in the initial rate of chloroform hydrolysis due to the intervention of the various halide ions and the nucleophilic constants of the halide ions according to Swain and Scott. These data rule out all of the alternate mechanisms which have been suggested.

The rates of basic hydrolysis of chloroform, dichloroiodomethane, dichlorobromomethane, chlorodibromomethane, and bromochlorofluoromethane have been determined in aqueous dioxane. The kinetics in all cases was first order in both haloform and hydroxide ion. The relative reactivity toward sodium hydroxide in aqueous dioxane was found to be

$$HCBrClF > HCCl_2Br > HCClBr_2 > HCCl_2I > HCCl_3 > HCF_3.$$

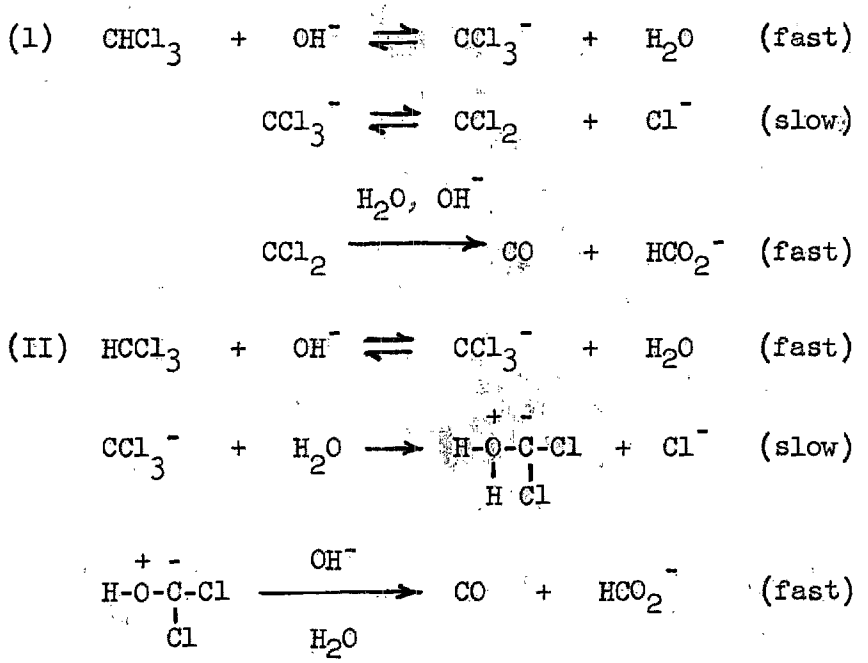
Heats and entropies of activation have been calculated from the observed rate constants.

THE MECHANISM OF THE BASIC HYDROLYSIS OF HALOFORMS

CHAPTER I

INTRODUCTION

Although Geuther (1) was probably the first to suggest that carbon dichloride is an intermediate in the basic hydrolysis of chloroform, the first good evidence for the existence of this compound as an intermediate was presented by Hine (2) as the result of a kinetic study of the basic hydrolysis of chloroform in aqueous dioxane. From the second order kinetics of the reaction (first order in both chloroform and hydroxide ion), three possible mechanisms were suggested:



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1. A. Geuther, Ann., 123, 121 (1862).
2. J. Hine, J. Am. Chem. Soc., 72, 2438 (1950).

$$(III)\quad HCCl_3 + OH^- \longrightarrow HCCl_2OH + Cl^- \qquad \text{(slow)}$$

$$HCCl_2OH \xrightarrow[OH^-]{H_2O} CO + HCO_2^- \qquad \text{(fast)}$$

Hine was able to present considerable evidence in support of mechanism I. The reversible formation of the trichloromethyl carbanion was supported by the fact that Sakamoto (3) found that the base catalyzed deuterium exchange of chloroform is rapid compared to the rate of hydrolysis. (Recent work in this laboratory (4) on the rate of base catalyzed deuterium exchange of haloforms in aqueous solution has confirmed Sakamoto's findings.)

The rate determining step, the loss of a chloride ion by an S_N1 reaction is reasonable when it is considered that the accumulation of halogens on the same carbon atom causes increased S_N1 reactivity (5,6), probably by resonance stabilization of the carbonium ion. It is to be expected that the trichloromethyl carbanion with its negative charge

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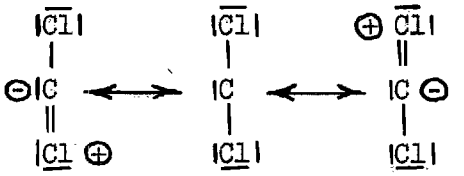
3. Y. Sakamoto, J. Chem. Soc. Japan, 57, 169 (1936); Bull. Chem. Soc. Japan, 11, 627 (1936); C. A. 31, 931 (1937).

4. J. Hine, R. C. Peek, Jr. and B. D. Oakes, unpublished work, Georgia Institute of Technology.

5. S. C. J. Olivier and A. P. Weber, Rec. trav. chim., 53, 869 (1934).

6. J. Hine and D. E. Lee, J. Am. Chem. Soc., 73, 22 (1951).

would lose a chloride ion easier than the neutral molecule of chloroform. The resultant carbon dichloride would have considerable resonance stabilization from contributing structures such as



Still more resonance stabilization would result if one allows ten-electron structures of chlorine.

Although it was not possible to rule out mechanism II completely, there were a number of reasons for considering it unlikely. One objection raised was that it requires the trichloromethyl anion to be more reactive than chloroform toward water, in spite of the fact that the negative end of the H-O dipoles in a water molecule must attack a negative carbon atom in the case of the anion.

Objections presented against mechanism III included the high reactivity of chloroform toward S_N2 attack by the strongly basic hydroxide ion and yet normal reactivity toward piperidine (2,7) when compared to the other chlorides of methane. Mechanism III does not show why the addition of hydroxide ions greatly increases the rate of reaction of thiophenoxide ion with chloroform to yield phenyl orthothioformate.

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7. P. Petrenko-Kritschenko and V. Opotsky, Ber., 39B, 2131 (1926).

Recent work of Singley (8) indicates it is very probable that bromoform, bromodichloromethane, dibromochloromethane, and fluorobromochloromethane undergo basic hydrolysis by the same mechanism as chloroform.

The purpose of this study is to determine the actual mechanism of the basic hydrolysis of chloroform.

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8. J. E. Singley, Jr., Carbon Dihalides as Intermediates in the Basic Hydrolysis of Haloforms, Unpublished M. S. Thesis, Georgia Institute of Technology, 1952.

CHAPTER II

METHOD OF ATTACK

It has been demonstrated by the work of Bateman, Hughes, and Ingold (9) on the effect of added salts upon the rate of solvolysis of p,p'-dimethylbenzhydryl chloride in aqueous acetone that the loss of the chloride ion to form the carbonium ion is reversible, the rate being specifically reduced by the addition of chloride ion. This is termed a mass or mass law effect[1], and the possibility of its observation increases with increasing stability of the carbonium ion and increasing nucleophilicity of the common ion.

It is believed that there was a fair chance of observing a mass law effect in the basic hydrolysis of chloroform if mechanism I were correct because of the S_N1 reaction in the second step:

$$CCl_3^- \rightleftharpoons CCl_2 + Cl^-$$

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[1] For a discussion of mass law effect, see C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Ithaca, N. Y., 1953, pp. 360-71.

9. L. C. Bateman, E. D. Hughes, and C. K. Ingold, J. Chem. Soc., 1940, 974.

Accordingly, the first experiments were to determine the rates of basic hydrolysis of chloroform in the presence of several added salts. Sodium nitrate, potassium nitrate, sodium chloride, sodium iodide, sodium perchlorate, and sodium fluoride were used at a concentration of 0.160 N. Since Hine (2) had observed specific salt effects in 66-2/3 per cent dioxane even at concentrations as low as 0.1 N, it was felt that pure water would be a better solvent than aqueous dioxane for the salt work.

In order to make the data more nearly comparable, rates were run in the presence of several salts at the same time in the same bath. In almost all cases, one of the salts was sodium chloride. For this reason, it is believed that the relative values of the rate constants are of much more accuracy than the average values.

As the rates of the reaction in the presence of sodium chloride and iodide were definitely lower than the presence of the inert salts such as sodium fluoride, perchlorate, and nitrate, it was evident that chloride and iodide ions were intervening. In agreement with the data of Hine (2), a higher rate in the presence of potassium ion was observed in the case of potassium nitrate. Since mechanism I has the loss of a chloride ion from the trichloromethyl anion as the rate determining step, it is not surprising to find that the nature of the added cation has some effect upon the rate of the reaction.

Even though it was evident that the three inert salts had very nearly the same effect upon the rate, it was considered worthwhile to work at salt concentrations of 0.080 normal. The salts used were the fluoride, chloride, bromide, iodide, nitrate, and perchlorate of sodium.

The fluoride, perchlorate, and nitrate ions all had approximately the same effect upon the rate, while the chloride, bromide, and iodide showed progressively greater decreases in the order given. In addition, the rate constants in the cases of the later two climbed with time, a behavior lending support to the intervention of both bromide and iodide ions as well as chloride with the intermediate carbon dichloride.

In order to prove this point, an attempt was made to isolate dichloroiodomethane from the reaction solution of chloroform and aqueous sodium hydroxide in the presence of sodium iodide. Although this attempt was successful, it was necessary to prove that dichloroiodomethane undergoes basic hydrolysis faster than does chloroform in order to demonstrate that the rate constants would be expected to rise with time according to mechanism I.

This work led logically into the determination of the rates of basic hydrolysis of chloroform and several other haloforms in various solvents and at several temperatures. Heats of activation as well as entropies of activation were calculated from the data.

Another problem along this line was the accurate determination of the fraction of the chloroform hydrolyzed that yielded formate ion. This is the factor f in the rate equation. A quantitative determination of formate ion in the presence of chloride ion based upon the titration of sodium formate with p-toluenesulfonic acid in methanol was devised and tested.

CHAPTER III

EXPERIMENTAL

Kinetic Runs

The kinetic runs at 35 and 14.3° were made in a large constant temperature water bath. The temperature was constant to within ± 0.05°, and from checking the temperature on a thermometer calibrated by the Bureau of Standards, it is believed that the temperature recorded is accurate to within 0.1°. It was necessary to circulate ice water through the cooling coils of the bath to maintain the setting at 14.3°.

The runs at 0° were made in an insulated icebox constructed from a five gallon can with one side cut out. It was supported in a plywood box in such a way as to allow for approximately 1-1/2 inches of sawdust insulation on all sides. An insulated top was provided. During the runs, the box was kept filled with a slurry of cracked ice and water. The temperature was constant to within 0.1°.

The multiple flask technique was used for the determination of the rate of basic hydrolysis of chloroform in the presence of added salts because of the low solubility of chloroform in water and its high vapor pressure at this temperature. Into each of several (generally twelve or more) 100 ml. Pyrex volumetric flasks was pipeted 80.0 ml. of either a 0.100 N or else a 0.200 N salt solution at bath temperature. The flask was then swept out with nitrogen, stoppered, and placed in the constant temperature bath. One-fourth of a milliliter of pure chloroform at room temperature was added to each flask by means of a

hypodermic syringe that was found to deliver 0.250 ± 0.0015 (average deviation) ml. The flask was restoppered, and the solution of the chloroform completed by vigorous shaking for about five minutes. The weight of the chloroform was calculated from the density of the chloroform at the temperature delivered. The flask was then returned to the constant temperature bath, and after about thirty minutes to allow thermal equilibration, the reaction was started by pipeting 20.0 ml. (at bath temperature) of standard sodium hydroxide solution into the flask. The entire contents of a single flask were used for a single point. A zero point was run after one or two minutes; the elapsed times, concentrations and the titers to back-titrant base were corrected to this zero point. To take a single point, a flask was removed from the bath, wiped dry with a clean towel, and the contents of the flask were quantitatively transferred to an Erlenmeyer flask containing a measured volume of a standard acid (an excess of aqueous p-toluenesulfonic acid to stop the reaction). The excess acid was back-titrated to the phenolphthalein end point with standard sodium hydroxide solution. The time for the end of the reaction was taken as the mid-point of the addition of the contents of the flask to the standard acid solution. The rate constants were calculated for each point from the following integrated rate expression:

$$k = \frac{2.303}{t(za-b)} \log \frac{b(a-x)}{a(b-zx)}$$

$z = 3 + f$
t = the time in seconds
a = the initial concentration of chloroform in moles/liter
b = the initial concentration of base in moles/liter
f = the fraction of chloroform yielding formate
x = the change in chloroform concentration during time t
k = the specific rate constant in liter-second^{-1} moles^{-1} of chloroform.

In every case, at least two different salts, one of which was usually sodium chloride, were run in the same bath at the same time. In this way a check was maintained between two different runs so as to allow close comparison of all results.

For the kinetic runs in 67 per cent dioxane at 35.0°, the reaction was followed by the withdrawal of 20.0 ml. samples from a reaction mixture prepared by pipeting the following into a 250 ml. volumetric flask:

1. 62.0 ml. of 0.09542 N sodium hydroxide;
2. 1.00 ml. of a mixture of 1.00 ml. of dioxane and 1.00 of 0.09542 N sodium hydroxide;
3. 20.0 ml. of boiled distilled water;
4. 155.0 ml. of dioxane.

After thermostating for thirty minutes or longer, the reaction was started by adding by pipet 12.00 ml. of a standard haloform solution in dioxane. The final volume of such a solution was found to be 246.3 ml. at 35.0°C. After shaking and replacing the flask in the bath, 20.0 ml. samples were withdrawn, and the reaction stopped by allowing the sample to drain into a measured volume of standard p-toluenesulfonic acid. The excess acid was back-titrated to the phenolphthalein end point with standard sodium hydroxide solution. The first point taken was used as a zero point, and all times and concentrations were corrected accordingly. Times were measured to the nearest second from the time of half-drainage of the pipets.

For the kinetic runs in 40 per cent dioxane at 35.0°, the only

departure from the foregoing technique was in the preparation of the solvent. This required the following additions to the flask:

1. 88.0 ml. of dioxane;
2. 88.0 ml. of water;
3. 62.0 ml. of the standard base;
4. 12.00 ml. of the standard haloform solution in dioxane.

The total volume of such a solution was 245.3 ml.

It was necessary to modify this procedure for use at 0° because dioxane is a solid at this temperature. The procedure used was to mix, at room temperature, a measured volume of the standard base with twice its measured volume of pure dioxane. To this solution was added a measured volume of 66-2/3 per cent dioxane at 0°, and finally, to start the reaction, a measured volume of a standard haloform solution in 66-2/3 per cent dioxane. In order to prevent a change in the nature of the solvent as result of the difference in the thermal contractions between dioxane and water, all of the 66-2/3 per cent dioxane was prepared by mixing two volumes of pure dioxane and one volume of boiled distilled water at room temperature. This solution was then chilled to 0° and used as required. The samples were withdrawn in chilled pipet and delivered into flasks containing cracked ice and excess standard acid. Data are given in Table 1.

Table 1. Preparation of Runs

Ml. of 0.09522 N Base	Ml. of Dioxane	Ml. of 66-2/3 Per Cent Dioxane	Ml. of Haloform Solution	Final Volume	Run
50.0	100.0	95.0	4.00	242.0	AI, AJ
65.0	130.0	40.0	20.00	246.9	AU, AV, AW, AX

The same technique as used for Runs AU through AX was used for Runs BB and BG, except that the last two solutions were delivered at 14.3 rather than 0°.

In addition, it was desirable for a number of reasons to use special techniques for some of the runs. A description of these follows.

For Runs AE and AF in 40 per cent dioxane at 0°, 60.0 ml. of standard base and 40.0 ml. of dioxane were mixed at room temperature. After cooling to zero, 140 ml. of 40 per cent dioxane and 15.0 ml. of a standard haloform solution were added to give a final solution volume of 250.9 ml. at 0°.

For Runs AS, AT, AY, and AZ in water at 0°, a known quantity of chloroform and a measured volume of sodium hydroxide solution were shaken at 0° until solution was completed.

In Runs BC, BD, BE, and BF 200.0 ml. of approximately 0.037 N sodium hydroxide in 66-2/3 per cent dioxane was the solvent. One milliliter of the haloform (at 32°) was delivered by hypodermic syringe into the solvent. As in like cases, the quantity of the haloform was

calculated from its density at this temperature. The initial concentration of the alkali was determined by means of a zero point titration of a sample. Fifteen milliliter samples were used.

The sample withdrawal method was also used in Runs AO and AP, but due to the low solubility of dichloroiodomethane in water at 35°, low concentrations of sodium hydroxide were required; thus it was found necessary to use 80 ml. samples. The reaction solutions were prepared by delivering 0.20 ml. of dichloroiodomethane (0.4847 g. average) by hypodermic syringe into 950 ml. of boiled distilled water in a one liter volumetric flask. After solution of the haloform and thermal equilibration, the reaction was started by the addition of 50.0 ml. of standard sodium hydroxide.

For Run AN, the multiple flask technique was modified somewhat. One-fourth of a milliliter of bromochlorofluoromethane was added by hypodermic syringe to previously weighed 50 ml. volumetric flasks containing 40.0 ml. (measured at 0°) of boiled distilled water. The haloform was dissolved and its weight determined after again weighing the flask and its contents. The flask was chilled to 0°, and the reaction started by the addition of 10.0 ml. of standard sodium hydroxide at 0°.

For Runs BQ and BR, the multiple flask technique was changed only in the manner of starting and stopping the reaction. To start the reaction, twenty milliliters of a solution of sodium hydroxide and sodium p-thiocresolate was added to each flask. To stop the reaction, the contents of the flask were transferred to a one liter flask containing cracked ice. After titrating the sample to the thymolphthalein end point with p-toluenesulfonic acid, it was made acidic with glacial

acetic acid, and the p-thiocresol titrated with standard iodine solution.

Isolation of Dichloroiodomethane

Ten milliliters of pure chloroform was dissolved in 1.80 liters of boiled distilled water by shaking for nearly one hour. Two hundred milliliters of 1.38 N carbonate free sodium hydroxide was added, the solution shaken, and 60 g. of C. P. sodium iodide added. The solution of all components was completed by shaking, and the reaction vessel was placed in a water bath at 35° for 16-1/2 hours. The bath water was colored black to prevent photolytic decomposition.

The reaction mixture was extracted with three portions of methylene chloride. After two washes of the extract with distilled water, the combined extracts were dried over Drierite. Much of the methylene chloride was lost by vaporization during the washing process, hence the combined extracts totaled only 50 ml.

The bulk of the methylene chloride was removed at 90 mm. pressure, and the residue was fractionated through a small column 24 inches in length, 6 mm. in diameter, and packed with a tantalum wire spiral. A fraction exhibiting the characteristic iodine color boiled at 45.2° at 38 mm. yield 1.12 g.; d_4^{25} 2.3852; n_D^{25} 1.5774; M_r^D 29.31 (calculated 29.35). Auger (10) reported d_4^0 2.41 and b.p. 40° (30 mm.).

Using the same concentrations of sodium iodide, chloroform, and base as before, extracts from 100 ml. samples rapidly developed an iodine color in light. Crystals of iodine were deposited in the column

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10. M. V. Auger, Comp. rend., 146, 1037 (1908).

upon attempted distillation, but not enough product was obtained to isolate. Under exactly the same conditions except in the absence of the base, the extracts did not show any iodine color or yield any iodine containing compound.

Determination of the Factor *f*

The factor *f* is defined as the fraction of the chloroform undergoing hydrolysis that yields formate ion. The products of the basic hydrolysis of chloroform are carbon monoxide and formate anion.

$$CHCl_3 + 3\ NaOH \longrightarrow 3\ NaCl + CO + 2\ H_2O$$

$$CHCl_3 + 4\ NaOH \longrightarrow 3\ NaCl + NaHCO_2 + 2\ H_2O$$

Each mole of chloroform forming carbon monoxide uses three moles of base; each mole of chloroform yielding formate uses four moles of base. It is evident that

$$\frac{\text{moles of hydroxide used}}{\text{moles of chloroform used}} = 3 + f.$$

Thus it is possible to evaluate *f* by titrations to determine both the changes in halide and hydroxide concentrations. This was the method used by Hine (2).

It was found that sodium formate could be titrated as a base in methanol solution with standard *p*-toluenesulfonic acid (in methanol) using a fresh solution of *m*-cresolsulfonphthalein in methanol as an indicator. This method gave results accurate to within 0.4 per cent of known samples of sodium formate even in the presence of large quantities of chloride ion. Fluoride ion interfered.

Results of the determination of the value of f on the same samples by both methods are given below.

Table 2. Determination of f

Run	Value of the Factor f	
	p-Toluenesulfonic Acid Method	Hydroxide-Halide Method
34	0.1434	0.1713
35	0.1471	0.2009
36	0.1448	0.1856
37		0.1797
Average	0.1451	0.1844

Since the hydroxide-halide method of determining f requires taking the difference between two large numbers whereas the other method does not, it is believed that the value of f lies closer to 0.15 than to 0.18; therefore the value of 0.15 was used for all haloforms involving carbon dichloride as an intermediate. The values of f were determined at a base concentration of 0.14 N and a haloform concentration of 0.1 M in water, yet they are in good agreement with the values of f determined by Oakes (11) in water at base concentrations of 0.044 N and haloform concentrations of 0.027 M.

11. B. D. Oakes, unpublished work, Georgia Institute of Technology.

Isotopic Ratio in the Formate Produced

In an effort to learn what happens after the rate determining step in the basic hydrolysis of chloroform, it might be of value to run the reaction in a solvent containing equal quantities of normal and heavy water, and to determine the ratio of hydrogen of deuterium in the formate produced. The single proton of chloroform is lost in the first step of the carbon dichloride mechanism. Münzberg and Oberst (12) report only slight exchange of deuterium and hydrogen in formate ion in 0.1 normal sodium hydroxide solution at 100°. Therefore any deuterium in the formate must result from the reaction of an intermediate with solvent.

The first approach was through the pyrolysis of the sodium formate to sodium oxalate and hydrogen. However, it was found that even with the use of one per cent sodium hydroxide as a catalyst and under 4 mm. pressure at 310°, the yield of hydrogen never exceeded 91 per cent. Since there is no reason to believe that a mixture of normal and deutero formate will yield a representative sample of hydrogen and deuterium, this approach was abandoned.

It is possible to convert sodium formate to formic acid by treatment with a solution of trichloroacetic acid in carbon tetrachloride. It is hoped that the isotopic ratio might be gotten from infra-red absorption measurement at the C-H and C-D stretching frequencies on a carbon tetrachloride solution of formic acid. Unfortunately the trichloroacetic acid and formic acid interacted to such an extent that it

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12. F. K. Munzberg and W. Oberst, Z. physik. Chem., B31, 18 (1935).

was impossible to analyze for them quantitatively by infra-red at the stretching frequencies.

Since sodium formate is somewhat soluble in both methanol and ethanol, it might be possible to devise a method of analysis for normal and deutero sodium formate at higher wave lengths than the C-H and C-D stretching frequencies.

Preparation and Purification of Reagents

Dichloroiodomethane.--Dichloroiodomethane was prepared by the method of Auger (10) by heating 350 g. of mercuric chloride in intimate mixture with 550 g. of iodoform under a pressure of 100 mm. and collecting the distillate. The head temperature never exceeded 95°. A total of 222.4 g. of distillate was collected and fractionated through a Todd still at a reflux ratio of 8:1. Seventy milliliters of liquid boiling between 41.5 and 42° at 30 mm. was obtained. After the addition of approximately one per cent diphenylamine, the dichloroiodomethane was washed with water, and then with small amounts of saturated solution of sodium thiosulfate until the iodine color was discharged. After three washings with water the liquid was dried over Drierite, but due to the development of an iodine color, it was necessary to repeat the washing steps given above. It was distilled at 38 mm. (b.p. 47°) after again being dried. It was found necessary to add one per cent diphenylamine by weight to inhibit free radical decomposition. The material was stored in a brown bottle under nitrogen. The final yield of purified product was 133 grams.

Bromochlorofluoromethane.--Bromochlorofluoromethane was prepared accord-

ing to the method used by Hine and Singley (8). Two hundred grams of mercuric fluoride (0.836 mole) and 160 ml. of dibromochloromethane (1.86 mole) were placed in a three necked flask equipped with a mechanical stirrer and a reflux condenser through which water heated to 40° was circulated so as to allow the bromochlorofluoromethane to escape while the dibromochloromethane refluxed. A distilling head with thermometer was placed at the top of the reflux condenser, and the product condensed by means of a downward condenser through which was circulated iced water. The product was collected in two receivers, the first chilled in ice-water mixture and the second by means of dry ice and acetone. The vapors were led to a water spray tube for absorption.

After gentle heating for five hours, during which time an effort was made to keep the head temperature between 30 and 40°, the material in the receiver was removed, and the crude product purified by fractionation: yield 102.4 g. or 83.4 per cent; n_D^{25} 1.4143; b. p. 36.0-36.7°. Berry and Sturtevant (13) reported n_D^{25} 1.4144 and b.p. 36.11-36.18°.

Dioxane.--Commercial dioxane was purified by the method of Fieser (14),

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13. K. L. Berry and J. M. Sturtevant, J. Am. Chem. Soc., 64, 1599 (1942).

14. L. F. Fieser, "Experiments in Organic Chemistry," Part II, second edition, D. C. Heath and Co., New York, N. Y., pp. 368-369.

distilled under nitrogen, and stored in brown bottles. The boiling point was 101°C.

Chloroform.--Chloroform was purified by the method of Fieser (15) and distilled from phosphorus pentoxide under nitrogen. The product was stored under nitrogen in a brown bottle, and a stream of nitrogen was blown through it for a few minutes to remove phosgene and hydrogen chloride immediately before use: n_D^{25} 1.4432; b.p. 61°. Timmermans (16) reports n_D^{25} 1.4426 and b.p. 61.2°.

Dichlorobromomethane and Dibromochloromethane.--These two haloforms were purified by distillation under nitrogen after refluxing over phosphorus pentoxide. Dichlorobromomethane: n_D^{25} 1.4950, b.p. 88.0-88.5°; reported (17) n_D^{25} 1.4958, b.p. 90.1°. Dibromochloromethane: n_D^{25} 1.5450, d_4^{32} 2.411; b.p. 116.0-116.5°; Jacobsen and Neumeister (18) reported b.p. 118-120°.

Salts.--All of the salts used were of chemically pure grade and, except for drying, were used without further purification. Anhydrous sodium perchlorate was prepared from the monohydrate in a drying pistol by applying a gentle vacuum while heating by means of refluxing bromobenzene. After

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15. Fieser, op. cit., pp. 365-366.

16. J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., New York, N. Y., 1950, p. 220.

17. Timmermans, op. cit., p. 223.

18. O. Jacobsen and R. Neumeister, Ber., 15, 601 (1882).

the bulk of the water had been removed, the sodium perchlorate was removed, ground into a fine powder, and replaced in the pistol. The drying was completed over phosphorus pentoxide under vacuum while heated by the refluxing bromobenzene.

Sodium Hydroxide Solution.--Carbonate free sodium hydroxide solution was prepared by two different methods. The 0.1776 N solution used for the work at salt concentrations of 0.160 N was prepared by dilution of a 1.4 N solution of sodium hydroxide that had been saturated with barium hydroxide. The 0.09542, 0.09422 and 0.02696 N solutions of sodium hydroxide that were used for all other work were made by diluting a quantity of filtered 50 per cent sodium hydroxide solution with boiled distilled water. This was done under nitrogen to prevent absorption of carbon dioxide. All solutions were standardized against potassium acid phthalate using phenolphthalein as an indicator. They were stored in polyethylene bottles.

p-Toluenesulfonic Acid.--p-Toluenesulfonic acid was prepared by dissolving the monohydrate in water and standardizing the solution against standard sodium hydroxide solution.

CHAPTER IV

DISCUSSION OF RESULTS

Effect of Added Salts

The effect of added salts at a concentration of 0.160 N upon the rate of basic hydrolysis of chloroform are tabulated below.

Table 3. Rate Constants for the Basic Hydrolysis of Chloroform in the Presence of 0.160 N Added Salts and 0.0353 N NaOH

Run	$k \times 10^4$ l. $mole^{-1}$ $second^{-1}$					
	NaCl	$NaNO_3$	$NaClO_4$	NaF	NaI	KNO_3
A	2.13					2.67
B	1.98	2.32				
D	2.19				1.00[a]	
F	2.06		2.37	2.32		

[a]Initial rate constant (extrapolated)

The climbing of rate constants with time in the presence of sodium iodide is illustrated in Fig. 1.

It is evident that sodium chloride and sodium iodide reduce the rate, but an examination of the rate constants shows that while the nature of the cation has a specific effect upon the rate, the differences in rates between the various anions (other than chloride and iodide) are not large and may be due solely to experimental error.

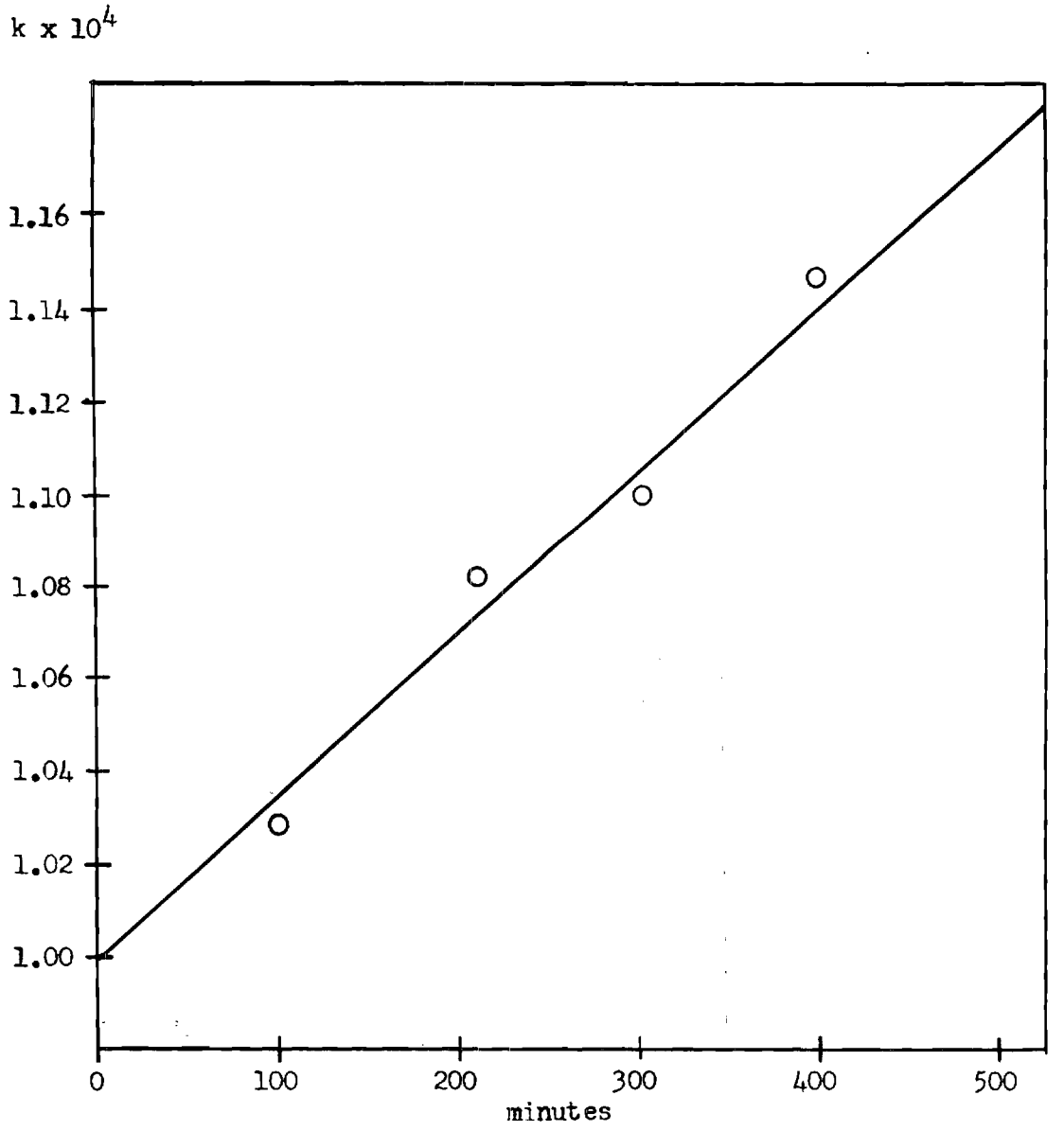

Fig. 1. Rate of Hydrolysis of Chloroform in the Presence of 0.160 N NaI and 0.0353 N NaOH

Since the rate constant ratios in Table 4 were calculated from data determined in the same baths at the same time, they allow better comparison between different runs than do the average rate constants.

Table 4. Rate Constant Ratios for the Hydrolysis of Chloroform in the Presence of 0.160 N Added Salts and 0.0353 N NaOH

Salt	Rate Constant Ratios[a]
Sodium Chloride	1.00
Sodium Fluoride	1.13
Sodium Perchlorate	1.15
Sodium Nitrate	1.16
Potassium Nitrate	1.25

[a]Compared to sodium chloride

The work with 0.160 N salt solutions was all carried out with alkali containing barium ions and therefore is not directly comparable to the runs at salt concentrations of 0.080 N, since these were made in the absence of barium ions.

The following data were determined at salt concentrations one-half of the former.

Table 5. Rate Constants for the Hydrolysis of Chloroform in the Presence of 0.080 N Added Salts and 0.19 N NaOH

Run	$k \times 10^4$ l. mole^{-1} second^{-1}					
	NaCl	NaF	$NaNO_3$	$NaClO_4$	NaI	NaBr
L	2.15			2.29	1.39[d]	
BH[a], BI[a], BJ[a]		2.39	2.38			1.95[d]
BK[b], BL[b], BM[b]	2.16			2.35		1.90[d]
BN[c], BO[c], BP[c]		2.37	2.39			1.95[d]

[a,b,c]Denotes runs made in the same bath at the same time

[d]Initial rate constant (extrapolated)

The climb of the rate constants with time in the presence of sodium bromide and iodide is illustrated in Fig. 2 and Fig. 3. It is evident that the initial rate of hydrolysis of chloroform is decreased by the addition of chloride, bromide, and iodide ions, and that the magnitude of the effect increases in the order given.

From a consideration of the results of the salt work, it seems evident that chloride, bromide, and iodide ions are intervening since the initial rate constants in the presence of these ions are materially less than in the presence of the ions which possess little or no nucleophilicity. According to mechanism I,

$$CCl_3^- \longrightarrow CCl_2 + Cl^-$$

$$CCl_2 + X^- \longrightarrow CCl_2X^-$$

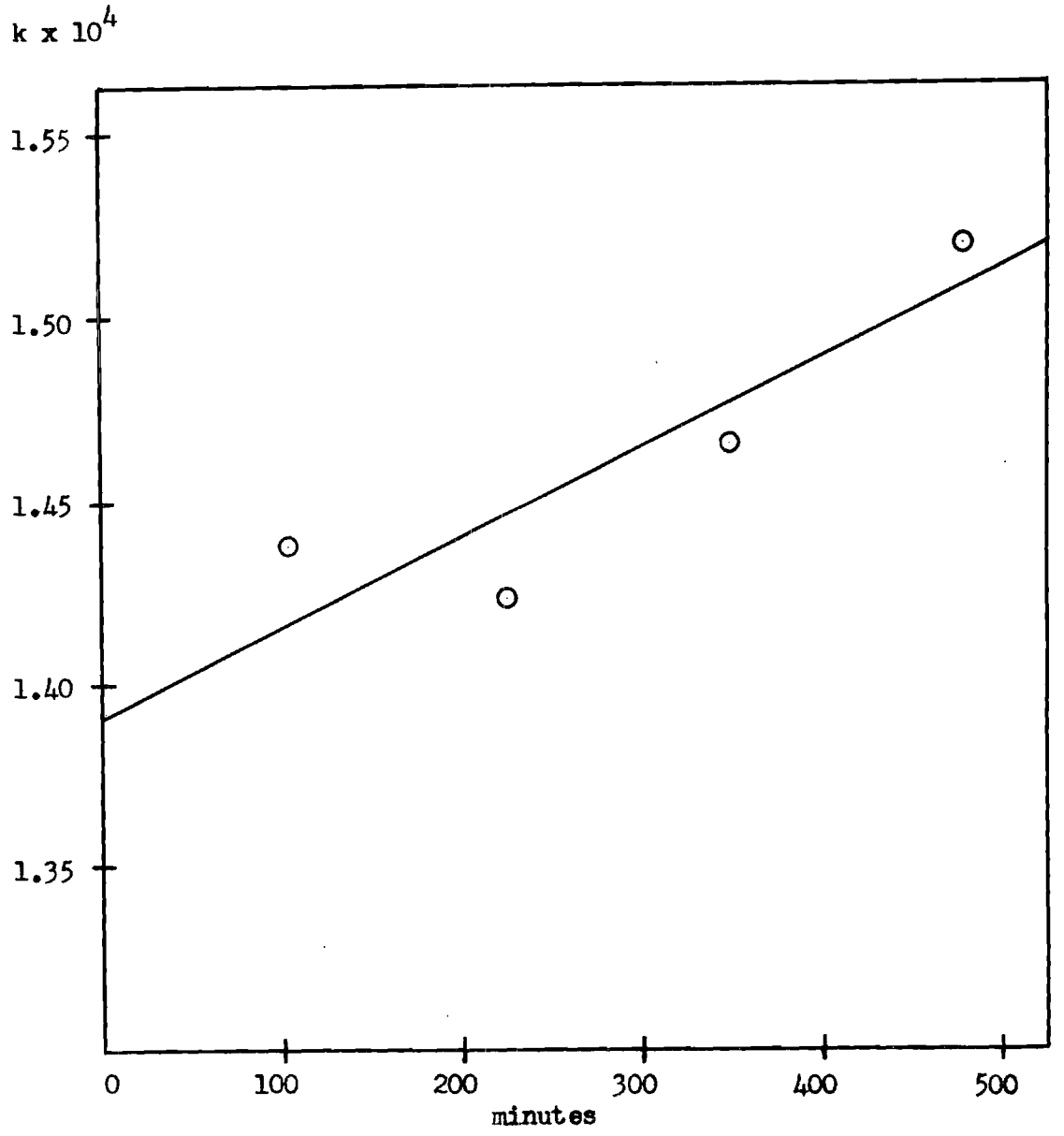

Fig. 2. Rate of Hydrolysis of Chloroform in the Presence of 0.080 N NaI and 0.019 N NaOH

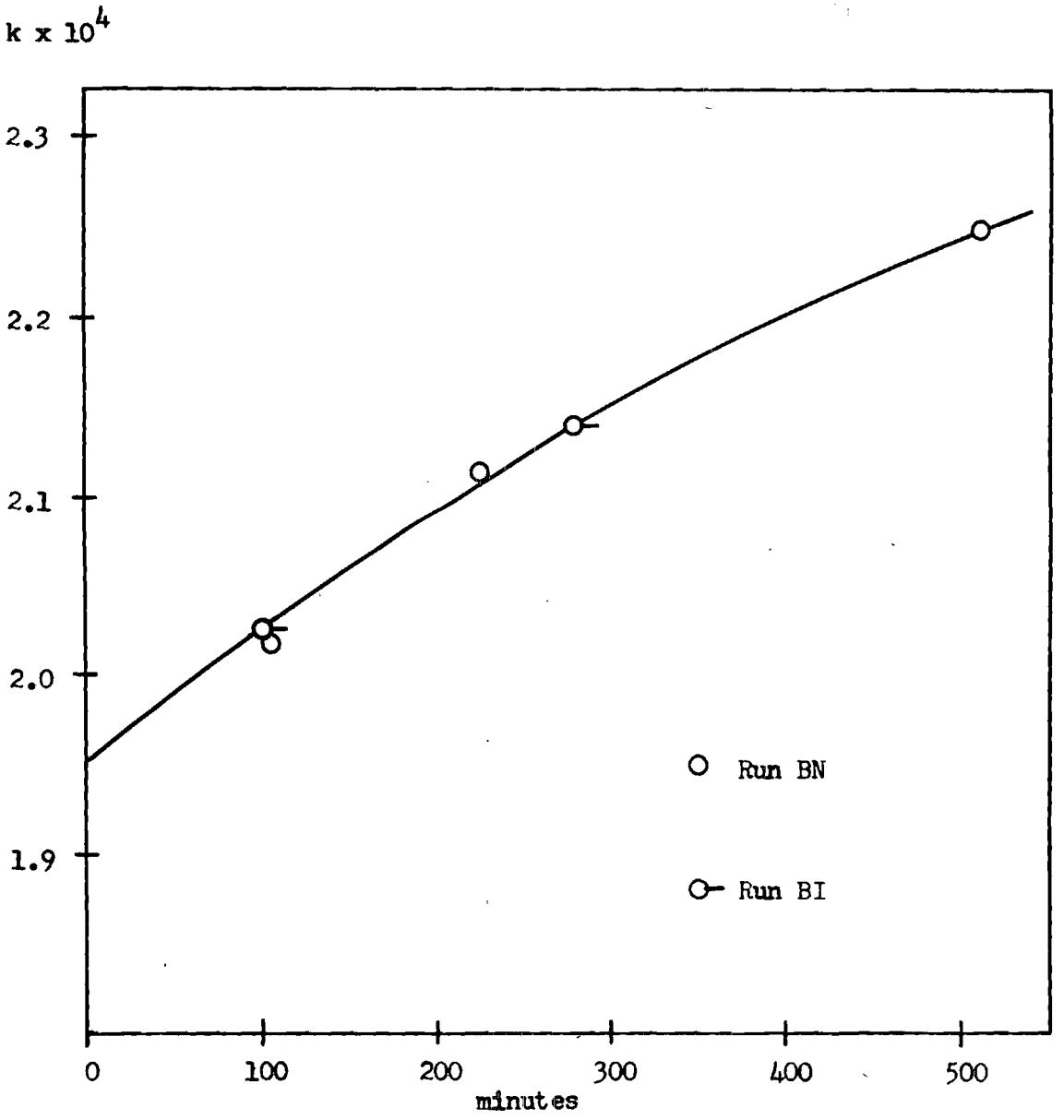

Fig. 3. Rate of Hydrolysis of Chloroform in the Presence of 0.080 N NaBr and 0.019 N NaOH

where X^- is the intervening ion. It is evident that the overall rate of the reaction will be reduced as the result of this intervention, since a fraction of the carbon dihalide is reverted to haloform.

When X^- is chloride ion, the second step simply becomes the reversal of step one, and a true mass law effect is observed. However, in the case of bromide and iodide ions, dichlorobromo- and dichloroiodomethane would be formed, and since these compounds hydrolyze faster than chloroform, the rate constants would climb with time. Proof of the formation of dichloroiodomethane was offered by the isolation of this compound from the reaction solution of chloroform with aqueous sodium hydroxide in the presence of sodium iodide.

Since the rate of reaction of chloroform is equal to $k_2 [CCl_3^-]$ in the absence of any added salts, the initial rate in the presence of an added salt that intervenes may be expressed as equal to $k_2 [CCl_3^-] \cdot q$, where q is the fraction of the carbon dichloride that does not revert to CCl_3^- or CCl_2X^-.

Using k_o to designate the rate constant at zero time for chloroform in the presence of an added nucleophilic ion, and k_g for the rate constant in the presence of an inert salt at the same ionic strength, it is apparent that

$$\frac{k_o}{k_g} = q$$

However, it may be shown that

$$q = \frac{k_w[H_2O] + k_h[OH^-]}{k_w[H_2O] + k_h[OH^-] + k_x[X^-]}$$

where k_w, k_h, and k_x are the specific second order rate constants for the reaction of carbon dichloride with water, hydroxide ion, and halide ion respectively.

Therefore,

$$\frac{k_o}{k_g} = \frac{k_w[H_2O] + k_h[OH^-]}{k_w[H_2O] + k_h[OH^-] + k_x[X^-]}$$

$$\frac{k_o}{k_g} = \frac{[H_2O] + \frac{k_h}{k_w}[OH^-]}{[H_2O] + \frac{k_h}{k_w}[OH^-] + \frac{k_x}{k_w}[X^-]}$$

To correlate the rates of reaction of various nucleophilic reagents with different substrates, Swain and Scott (19) have devised the relationship $\log k/k_o = s\,n$. In this equation k is the second order rate constant for the reaction of a given nucleophilic reagent with a given substrate, n is the specific nucleophilic constant for that reagent, s is a constant related to the substrate's ability of discriminate between various nucleophilic reagents, and k_o is the second order rate constant for the reaction of the substrate with water.

It is evident that Swain and Scott's k/k_o have the same significance as our k_h/k_w and k_x/k_w.

Designating the ratios as corresponding α's,

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19. C. G. Swain and C. B. Scott, J. Am. Chem. Soc., 75, 141 (1953).

$$\frac{k_o}{k_g} = \frac{[H_2O] + \alpha_h[OH^-]}{[H_2O] + \alpha_h[OH^-] + \alpha_x[X^-]} \quad (1)$$

From Swain and Scott's equation we may write

$$\frac{\log \alpha_1}{\log \alpha_2} = \frac{n_1}{n_2} \quad (2)$$

where n_1 and n_2 are specific nucleophilic constants. Swain and Scott give values of $\underline{n}$ as 3.04 ± 0.09, 3.89 ± 0.09, 4.20 ± 0.15, and 5.04 ± 0.21 for chloride, bromide, hydroxide, and iodide ions respectively (compared to water as 0.00).

The value of k_o for chloroform in the presence of 0.080 $\underline{N}$ sodium iodide was found by extrapolation of the data of Run L (see Fig. 2) to zero time to be 1.39×10^{-4} liter mole^{-1} second^{-1}. At the same ionic strength of sodium perchlorate in the same run, a value of 2.287×10^{-4} may be assigned to k_g, thus making k_o/k_g equal to 0.608.

Extrapolation of the data of Runs BI and BN to zero time gave a value of 1.95×10^{-4} for k_o in the presence of 0.080 $\underline{N}$ sodium bromide, making k_o/k_g equal to 0.819 where k_g is 2.38×10^{-4} (see Fig. 3).

For the effect of 0.080 $\underline{N}$ sodium chloride, the data of Run L gives a value of k_o/k_g of 2.149 divided by 2.287 or 0.919, while that from Runs BL and BM gives a value of 2.163 divided by 2.353 or 0.939. The average of these two values is 0.929.

The $[H_2O]$ under these conditions is approximately 55.1.

Using these ratios of k_o/k_g and Swain and Scott's values of $\underline{n}$ for the halide and hydroxide ions, equations (1) and (2) were solved

together to yield values of α_h and α_x for each halide ion. The three different values of α_h were averaged (α_h average equals 229), and new values of α_x were then calculated for chloride, bromide, and iodide using the average values of α_h. Although work was not done at enough concentrations of hydroxide to state that Swain and Scott's value of n for hydroxide holds for our work, it is evident from rearranging equation (1)

$$\alpha_x = \frac{(1-q)}{q}\left[\frac{[H_2O] + \alpha_h[OH^-]}{[X^-]}\right]$$

that while the absolute values of α_x are dependent upon the value of α_h, the values of α_x for chloride, bromide, and iodide would have the same relative value regardless of the value of α_h used. Results are reported in Table 6.

Table 6. Values of α_x for Halide Ions with Carbon Dichloride at 0.080 N Added Salt and 0.019 N NaOH

Ion	α_x	log α_x	n
Iodide	480	2.681	5.04
Bromide	164	2.215	3.89
Chloride	56.8	1.754	3.04
Hydroxide	229	2.360	4.20

Using the average value of α_h determined from the work at 0.080 N salt concentrations, it is possible to calculate values of α_x for chloride and iodide ion from the data at salt concentrations of 0.160 N. The data and calculated values are recorded in Table 7.

Table 7. α_x at 0.160 N Salt and 0.0353 N NaOH

Run	Halide	$k \times 10^4$ k_o	k_g	k_o/k_g	α_x	$\log \alpha_x$
B	Chloride	1.98	2.32	0.856		
F	Chloride	2.06	2.35	0.876		
Average	Chloride			0.866	61.1	1.786
D	Iodide	1.00[a]	2.35	0.426	532	2.726

[a]Initial rate constant (extrapolated)

To test the results, the data of Tables 6 and 7 are plotted on Fig. 4. Log α versus n should yield a straight line.

From the density and percentage salt in a 1.5 M solution of sodium perchlorate at 35°, with the assumption that the addition of 0.2 mole of sodium chloride per liter causes the same decrease in water concentration in 1.5 M sodium perchlorate as it does in 1.5 N sodium chloride solution, it is possible to estimate the concentration of water in 1.5 M sodium perchlorate with 0.2 N added sodium chloride as 51.1 molar. Using this value, the data of Runs AK, AL, and AM, and α_h as 229, α_x was calculated for chloride and bromide ions. Data and calculated values are recorded below.

Table 8. α_x at 0.20 N Salt, 1.5 N $NaClO_4$ and 0.019 N NaOH

Run	Anion	$k \times 10^4$ k_o	k_g	k_o/k_g	α_x
AL	Perchlorate		1.978		
AM	Chloride	1.538		0.778	79.1
AK	Bromide	1.259[a]		0.571	158

[a]Initial rate constant (extrapolated)

It appears quite certain that the effects are due to intervention of the halide ions and not to specific salt effect in view of the agreement of the data to a straight line at salt concentrations of 0.080 and 0.160 N (see Fig 4). The same effects of chloride and bromide ions were observed even at a salt concentration of 0.2 N in 1.5 N sodium perchlorate solution, where specific salt effects would be "swamped" by the high concentration of electrolyte. Since the high salt concentration constitutes a different medium, one does not expect good agreement of α_x with the values of α_x at low electrolyte concentrations.

The slope of the line is 0.55, thus this is the value of s for carbon dichloride. The parameter s is related to the ability of the substrate to discriminate between various nucleophilic reagents; a high value of s indicates a high ability to discriminate. It has been shown by Hughes, Ingold, and co-workers (20) that the ability of a

20. L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, J. Chem. Soc., 1940, 979.

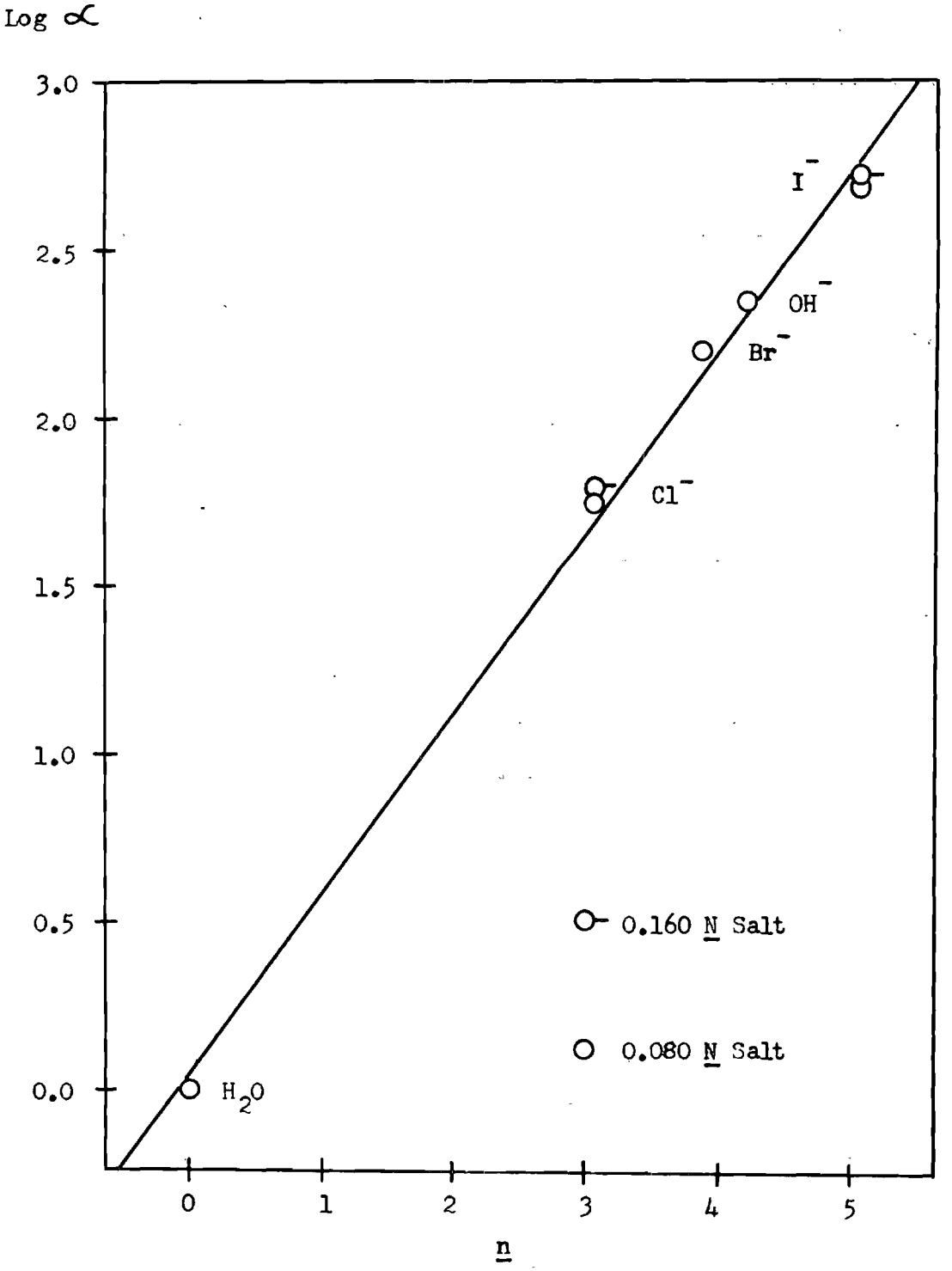

Fig. 4. Log ∝ versus n for Carbon Dichloride

reactive intermediate (in their case, carbonium ions) to discriminate between nucleophilic reagents increases with increasing stability of the intermediate. From the data of Swain, Scott, and Lohmann (21), a value of s of 0.55 may be estimated for the benzhydryl carbonion ion, a value very close to that for carbon dichloride. It is therefore reasonable to conclude that the benzhydryl carbonium ion and carbon dichloride are of comparable reactivity toward simple nucleophilic reagents.

In the original paper by Hine (2), two alternate mechanisms consistent with the second order kinetics were proposed in addition to the more likely carbon dichloride mechanism. (See page 2, Chapter I). It is possible to rule out both mechanism II and mechanism III on the basis of the results of the basic hydrolysis of chloroform in the presence of added salts.

From the data presented it is seen that the reduction in the rate of hydrolysis of chloroform in the presence of the added salts was of the order NaI > NaBr > NaCl, all of which rates are lower than the rate in the presence of an inert salt (NaF, $NaClO_4$, or $NaNO_3$). In addition, the rate constants in the presence of bromide or iodide ion climbed with time. These facts are consistent with the carbon dichloride mechanism, since a nucleophilic attack of halide ion upon the immediate carbon dichloride would cause a reduction in the overall rate of hydrolysis of the chloroform by reverting a part of the carbon dichloride to either CCl_3^- or CCl_2X^-. Since it has been shown that dichloroiodo-

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21. C. G. Swain, G. B. Scott, and K. H. Lohmann, J. Am. Chem. Soc., 75, 136 (1953).

methane and dichlorobromomethane react faster under the same conditions than does chloroform, it is to be expected that the rate constants would climb with time in the presence of bromide or iodide but not chloride ion because of the production of dichlorobromomethane and dichloroiodomethane. This view is entirely in accord with the base catalyzed radioactive chloride exchange of chloroform (22) and the isolation of dichloroiodomethane from a reaction solution of chloroform in aqueous sodium hydroxide and sodium iodide. Since dichloroiodomethane was not formed in the absence of the base, it is evident that this haloform did not result from an S_N2 attack of iodide ion upon chloroform. This is in agreement with the observed very low S_N2 reactivity of iodide ion upon chloroform in acetone solution (23).

In alternate mechanism II, intervention of halide ions would probably occur either as an S_N2 displacement of chloride ion from the intermediate CCl_3^- by halide ion, or by an S_N2 attack (with the displacement of water) of the halide ion upon the intermediate $H_2O^+\text{-}CCl_2^-$. The former would cause no change in the rate from the action of chloride ion, but an increase in the rate from the action of bromide or iodide ion since the rate of disappearance of CCl_3^- is thereby increased because of the conversion of a part of the CCl_3^- to an intermediate that will react faster than the original CCl_3^-.

The S_N2 attack of a halide ion upon $H_2O^+\text{-}CCl_2^-$ is extremely unlikely in view of the low stability of such an intermediate, especially

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22. J. Horiuti and K. Tanabe, Proc. Japan Acad., 27, 127 (1952).

23. J. Hine, unpublished work, Georgia Institute of Technology.

in basic solution. In actuality, it is an oxonium ion and should lose a proton to the hydroxyl ion present extremely rapidly or rearrange to $HO\text{-}CHCl_2$. In all probability, it would not exist long enough for added halide ion to show any effect other than a general salt effect upon the rate. Mechanism II may therefore be ruled out.

Mechanism III would predict an increase in the rate due to the conversion of part of the chloroform to a more reactive haloform in the presence of bromide or iodide ion. Therefore, mechanism III may be ruled out.

In Runs BQ and BR in the presence of sodium p-thiocresolate, some of the chloroform used yielded orthothioester, and since these molecules of chloroform use no alkali in going to the ortho ester, the decrease in chloroform cannot be determined by the change in hydroxide concentration alone. It is thus necessary to correct the instantaneous concentrations of chloroform used in calculating the rate constants for the amount of chloroform which yields orthothioester.

It is evident that the following relations are true

$$\Delta[OH^-] = \Delta[HCCl_3]\ (3+f)\ (1-p)$$

$$\Delta[p\text{-}CH_3C_6H_4S^-] = \Delta[HCCl_3]\ (3)\ (p)$$

where p is the fraction of chloroform yielding orthoester, and f is the fraction of chloroform that yields formate ion.

Thus, assuming that p is constant

$$\frac{\Delta[p\text{-}CH_3C_6H_4S^-]}{\Delta[OH^-]} = \frac{3p}{(3+f)\ (1-p)}\ .$$

A value for the left hand term of this equation was obtained by fitting the data of Runs BQ and BR to the equation

$$\left[\underline{p}\text{-}CH_3C_6H_4S^-\right] = m\left[OH^-\right] + c\ .$$

This must be true if $\underline{p}$ is constant. The slope $\underline{m}$ is equal to $\frac{\Delta\left[\underline{p}\text{-}CH_3C_6H_4S^-\right]}{\Delta\left[OH^-\right]}$ and was found by the method of least squares to be 0.1449. Solving for $\underline{p}$ using this value gives an answer of 0.132, making $(3+f)(1-p)$ equal to 2.734. This value is 0.65 per cent lower than the value gotten from the treatment of the data according to the method used by Hine (2). Although the higher value was used in calculating the rate constants in Runs BQ and BR, calculation of the rate constants on the basis of the lower value is not warranted in view of the fact that the value of $\underline{f}$ is probably higher in the presence of $\underline{p}$-thiocresolate ion than in its absence.

The actual rate was expressed as

$$\text{rate} = k\left[HCCl_3\right]\left[OH^-\right] \quad \text{or}$$

$$\frac{dx}{dt} = k\,(a-x)\left[b-(3+f)(1-p)x\right]\ .$$

Integration gives

$$k = \frac{2.303}{t\left[(3+f)(1-p)a-b\right]} \log \frac{b}{a}\left[\frac{(a-x)}{b-(3+f)(1-p)x}\right]\ .$$

Rate constants calculated in this manner are within experimental error of the rate constants in the absence of sodium $\underline{p}$-thiocresolate (at the same ionic strength of inert salt, however). Therefore it must be that the $\underline{p}$-thiocresolate ion intervenes after the rate determining step unless, as is very unlikely, a very large specific salt effect

exists for this ion.

Rates of Basic Hydrolysis of Haloforms

Rates of basic hydrolysis of some haloforms at different temperatures are tabulated below.

Table 9. Rates of Hydrolysis of Haloforms

Haloform	Solvent Per Cent Dioxane	Temp. °C.	$k \times 10^4$ liter $mole^{-1}$ $second^{-1}$
$HCCl_3$	67	35.00	3.192 ± 0.050
$HCCl_3$	40	35.00	3.309 ± 0.030
$HCCl_3$	0	35.00	2.412 ± 0.025
$HCCl_3$	66-2/3	0.0	0.01041 ± 0.00081
$HCCl_3$	0	0.0	0.00602 ± 0.00039
$HCCl_2I$	67	35.00	39.95 ± 0.37
$HCCl_2I$	40	35.00	22.94 ± 0.19
$HCCl_2I$	0	35.00	12.85 ± 0.84
$HCCl_2I$	66-2/3	0.0	0.1182 ± 0.0034
HCBrClF	66-2/3	0.0	190.4 ± 3.9
HCBrClF	40	0.0	88.95 ± 1.88
HCBrClF	0	0.0	15.31 ± 1.21
HCBrClF	66-2/3	14.3	2,146. ± 82
$HCCl_2Br$	66-2/3	0.0	0.3518 ± 0.0099
$HCClBr_2$	66-2/3	0.0	0.1374 ± 0.0031

It was found that fluoroform failed to react with aqueous sodium hydroxide to any detectable extent at 50°.

The relative order of reactivity toward sodium hydroxide is

$$HCBrClF > HCCl_2Br > HCClBr_2 > HCCl_2I > HCCl_3 > HCF_3.$$

A consideration of the carbon dihalide mechanism reveals that there are two important factors that affect the rate of reaction. These are the acidity of the haloform and the ease of loss of the halide ion from the trihalomethyl carbanion.

The acidity of the haloform is dependent upon the electronegativity of the halogens attached to the carbon and the resonance stabilization of the trihalomethyl anion, as well as possible steric factors. On the basis of the inductive effect alone, we would expect the acidity of the haloforms to decrease in the order in which the electronegativity of the halogens attached to the carbon decreases. This would make the order fluoroform, chloroform, bromoform, and iodoform. However, resonance stabilization of the trihalomethyl carbanion can result from ten-electron structures of chloride and bromine, but not fluorine because of the unavailability of d orbitals in the last case. This is in agreement with the work of Sherman and Bernstein (24), who found in a heterogeneous system that the hydrogen-deuterium exchange of dibromochloromethane proceeds more rapidly than does that of dichlorobromomethane, and with the results of workers in this laboratory (4), who

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24. R. H. Sherman and R. B. Bernstein, J. Am. Chem. Soc., 73, 1376 (1951).

found that deuterobromoform in a homogeneous system exchanged approximately 120 times faster than deuterochloroform. Although sufficient data is not available to make a definite statement, it does seem as though the resonance stabilization of the trihalomethyl carbanion by utilization of the d orbitals of the halogens is more important than the electronegativity of the halogens in determining the acidity of the haloform. It also appears that bromine may be more effective in stabilizing a carbanion than is chlorine.

The relative rates for dichlorobromomethane, dibromochloromethane, and chloroform suggest that α-chlorine is better at stabilizing carbonium ions than is α-bromine, and that a bromide ion is more easily lost than a chloride ion by S_N1 reaction. This is in accord with the work of Hine and Lee (6) who found the same relative order of S_N1 reactivity among the benzotrihalides.

A comparison of the rates for chloroform, dichlorobromomethane, and dichloroiodomethane is of interest. It is expected that the S_N1 reactivity of the trihalomethyl anions would be in the order $CCl_2I^- > CCl_2Br^- > CCl_3^-$. Therefore, the reversal in the order of reactivity of the iodo- and the bromo- compounds must be due to the difference in the acidities of the corresponding haloforms. We may thus predict that dichlorobromomethane is a stronger acid than is dichloroiodomethane.

The reasons for the high reactivity of the bromochlorofluoromethane are not known. The author believes that both an α-fluorine and an α-chlorine may lead to anomalously high S_N1 reactivity for another halogen on the same carbon atom.

Heats and entropies of activation for the reaction of the

haloforms with sodium hydroxide were calculated from the absolute rate equation (25),

$$k = \frac{KT}{h} e^{-\frac{\Delta H^I}{RT}} e^{\frac{\Delta S^I}{R}},$$

Table 10. Heats and Entropies of Activation for Haloforms

Haloform	Per Cent Dioxane in Solvent	$k \times 10^4$ 0°	$k \times 10^4$ 35.0°	ΔH^I Kcal.	ΔS^I e. u.
$HCCl_3$	0	0.00602	2.412	28.0	+15.9
$HCCl_3$	67	0.01041	3.192	26.8	+12.3
$HCCl_2I$	67	0.118	39.95	27.2	+18.8
HCBrClf	66-2/3	190.44	2,146[b]	25.8	+28.4
$HCClBr_2$	66-2/3	0.1373	40.0[c,d]	26.0	+14.8
$HCCl_2Br$	66-2/3	0.3515	86.5[c,d]	25.3	+13.8

[b]Temperature 14.3°

[c]Temperature 35.7°

[d]From the work of J. E. Singley (8)

The probable error based upon the average deviations in the rate constants was less than 0.6 Kcal for ΔH^I and about 2 e. u. for ΔS^I.

25. S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of of Rate Processes." Mc-Graw-Hill Book Co., Inc., New York, N. Y. 1941, p. 14.

From the above data it is evident that fluorobromochloromethane reacts faster than the other haloforms because of both entropy and heat of the activation effects.

In the cases three of the haloforms (chloroform, dichloroiodomethane, and bromochlorofluoromethane) it was found that the rate of reaction increased with the percentage dioxane in the solvent. This is certainly due to the effect of the solvent upon the first step equilibrium.

CHAPTER V

CONCLUSIONS

It has been shown, upon the basis of intervention effects of chloride, bromide, and iodide ions, that the mechanism of the basic hydrolysis of chloroform, and probably also dichloroiodomethane, dichlorobromomethane, dibromochloromethane, and bromochlorofluoromethane, proceeds neither by mechanism II nor III, but probably by one involving the trihalomethyl carbanion and carbon dihalide as intermediates.

By the use of relative rate constants, the results of the intervention of halides ions with carbon dichloride have been quantitatively correlated with nucleophilicity constants for the halide ions.

The relative order of reactivity toward sodium hydroxide was found to be:

$$HCBrClF > HCCl_2Br > HCClBr_2 > HCCl_2I > HCCl_3 > HCF_3 .$$

Heats and entropies of activation have been calculated and are recorded in Table 10.

APPENDIX

Table 11. Standard Haloform Solutions

No.	Haloform	Concentration (g./ml.)	Temp.	Solvent Per Cent Dioxane	Run	Volume Used ml.
A	$HCCl_3$	0.07187	35°	100	M	5
1	$HCCl_2I$	0.12334	35	100	R	12
2	$HCCl_2I$	0.11617	35	100	P	12
3	$HCCl_2I$	0.12525	35	100	S, X	12
4	$HCCl_2I$	0.11578	35	100	T	12
5	$HCCl_3$	0.06740	35	100	U	12
6	$HCCl_3$	0.07118	35	100	V	12
7	$HCCl_2I$	0.14217	35	100	W, Y	12
8	$HCCl_2I$	0.13075	35	100	AA	12
11	$HCCl_3$	0.07991	35	100	AE	12
12	$HCCl_3$	0.08216	35	100	AF	12
13	$HCCl_3$	0.08483	35	100	AG	12
14	HCBrClF	0.09604	0	66 2/3	AI	4
16	HCBrClF	0.07697	0	66 2/3	AJ	4
17	HCBrClF	0.02358	0	40	AQ	15
18	HCBrClF	0.02179	0	40	AR	15
19	$HCCl_3$	0.04487	0	66 2/3	AU	20
20	$HCCl_3$	0.04599	0	66 2/3	AV	20
21	$HCCl_2I$	0.07338	0	66 2/3	AW	20
22	$HCCl_2I$	0.07178	0	66 2/3	AX	20
24	HCBrClF	0.01539	14.3	66 2/3	BB, BG	20

Table 12. Run A. Chloroform in the Presence of 0.160 N Added Salt at 35.0°

Point	Added Salt	Time Minutes	Delta Titer ml.	k x 10^4 l.mole^{-1}sec.$^{-1}$
1	NaCl	124	2.60	2.10
2	NaCl	296	5.46	2.10
3	NaCl	909	11.93	2.17
4	NaCl	986	12.45	2.17
Average	NaCl			2.13 ± 0.035
6	KNO_3	114	2.97	2.67
7	KNO_3	276	6.38	2.73
8	KNO_3	900	13.06	2.62
9	KNO_3	964	13.57	2.67
Average	KNO_3			2.67 ± 0.030

a = 0.03065 b = 0.03374 f = 0.15

Infinite delta titer 19.0 ml. of 0.1776 N NaOH

Table 13. Run B. Chloroform in the Presence of 0.160 N Added Salts at 35.0°

Point	Added Salt	Time Minutes	Delta Titer ml.	k x 10^4 l.mole^{-1}sec.$^{-1}$
1	NaCl	99	2.10	1.95
2	NaCl	180	3.56	1.93
3	NaCl	284	5.37	2.02
4	NaCl	410	7.18	2.02
12	NaCl	472	7.93	2.00
Average	NaCl			1.98 ± 0.036
6	$NaNO_3$	92	2.29	2.32
7	$NaNO_3$	175	4.04	2.32
8	$NaNO_3$	278	5.87	2.37
9	$NaNO_3$	408	7.93	2.32
10	$NaNO_3$	530	9.20	2.25
Average	$NaNO_3$			2.32 ± 0.022

a = 0.03095 b = 0.03528 f = 0.15

Infinite delta titer 19.9 ml. of 0.1776 N NaOH

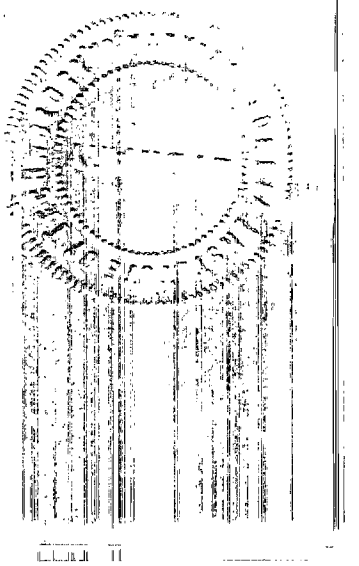

Table 14. Run D. Chloroform in the Presence of 0.160 N Added Salts at 35.0°

Point	Added Salt	Time Minutes	Delta Titer ml.	k x 10^4 l.mole^{-1}sec.$^{-1}$
4	NaCl	100	2.30	2.15
8	NaCl	100	2.28	2.15
3	NaCl	218	4.60	2.18
7	NaCl	215	4.61	2.19
2	NaCl	309	6.30	2.27
6	NaCl	306	6.15	2.22
1	NaCl	400	7.38	2.17
5	NaCl	402	7.57	2.22
Average	NaCl			2.19 ± 0.035
12	NaI	100	1.15	1.028
11	NaI	212	2.42	1.082
10	NaI	303	3.40	1.100
9	NaI	400	4.49	1.147
Initial	NaI (Extrapolated)			1.00

a = 0.03089 b = 0.03527 f = 0.15

Infinite delta titer 19.9 ml. of 0.1776 N NaOH

Table 15. Run F. Chloroform in the Presence of 0.160 N Added Salts at 34.9°

Point	Added Salt	Time Minutes	Delta Titer ml.	$k \times 10^4$ l.mole^{-1}sec.$^{-1}$
1	$NaClO_4$	99.5	2.43	2.45
2	$NaClO_4$	239.0	5.17	2.33
3	$NaClO_4$	426.0	8.29	2.40
4	$NaClO_4$	562.5	9.71	2.28
Average	$NaClO_4$			2.37 ± 0.06
5	NaF	95.0	2.30	2.40
6	NaF	237.5	5.05	2.28
7	NaF	423.0	8.16	2.37
8	NaF	558.5	9.45	2.22
Average	NaF			2.32 ± 0.07
9	NaCl	92.0	1.93	2.08
10	NaCl	233.5	4.57	2.07
11	NaCl	420.5	7.26	2.03
12	NaCl	555.0	8.92	2.03
Average	NaCl			2.06 ± 0.02

a = 0.03122 b = 0.03552 f = 0.15

Infinite delta titer 20.0 ml. of 0.1776 N NaOH

Table 16. Run L. Chloroform in the Presence of 0.080 N Added Salts at 34.9°

Point	Added Salt	Time Minutes	Delta Titer ml.	k x 10^4 $l.mole^{-1}sec.^{-1}$
1	NaCl	100.0	2.31	2.135
2	NaCl	227.5	4.96	2.211
3	NaCl	351.0	6.95	2.174
4	NaCl	486.0	8.55	2.074
Average	NaCl			2.149 ± 0.042
5	$NaClO_4$	103.5	2.53	2.268
6	$NaClO_4$	225.0	5.00	2.259
7	$NaClO_4$	345.5	7.18	2.315
8	$NaClO_4$	481.5	9.16	2.308
Average	$NaClO_4$			2.287 ± 0.026
9	NaI	107.5	1.71	1.439
10	NaI	225.0	3.34	1.423
11	NaI	350.0	5.04	1.465
12	NaI	480.0	6.71	1.519
Initial	NaI (Extrapolated)			1.39

a = 0.03099 b = 0.01896 f = 0.15

Infinite delta titer 19.9 ml. of 0.09542 N NaOH

Table 17. Runs BH, BI, and BJ. Chloroform in the Presence of 0.080 N Added Salts at 35.0°

Point	Added Salt	Time Seconds	Delta Titer ml.	k x 10^4 l.$mole^{-1}$$sec.^{-1}$
1	NaF	6,000	2.49	2.396
2	NaF	15,720	5.76	2.387
3	NaF	18,360	6.56	2.395
Average	NaF			2.393 ± 0.004
6	NaBr	6,000	2.14	2.024
7	NaBr	16,620	5.53	2.139
8	NaBr	18,360	6.57	2.404
Initial	NaBr	(Extrapolated)		1.95
11	$NaNO_3$	6,000	2.45	2.350
12	$NaNO_3$	16,440	5.98	2.534[c]
13	$NaNO_3$	18,000	6.49	2.413
Average	$NaNO_3$			2.381 ± 0.031

a = 0.03057 b = 0.01863 f = 0.15

Infinite delta titer 19.6 ml. of 0.09522 N NaOH

[c]Not averaged

Table 18. Runs BK, BL, and BM. Chloroform in the Presence of 0.080 N Added Salts at 34.9°

Point	Added Salt	Time Seconds	Delta Titer ml.	k x 10^4 l.mole^{-1}sec.$^{-1}$
1	NaBr	6,000	7.14	1.907
2	NaBr	12,030	14.31	2.023
3	NaBr	18,900	21.23	2.095
4	NaBr	24,000	26.12	2.136
5	NaBr	29,370	30.07	2.115
Initial	NaBr	(Extrapolated)		1.90
6	NaCl	6,120	8.06	2.120
7	NaCl	12,000	15.17	2.195
8	NaCl	18,630	21.48	2.145
9	NaCl	24,000	26.61	2.190
Average	NaCl			2.163 ± 0.027
10	$NaClO_4$	6,030	8.71	2.351
11	$NaClO_4$	12,030	15.99	2.328
12	$NaClO_4$	18,510	23.18	2.375
13	$NaClO_4$	24,000	28.07	2.358
Average	$NaClO_4$			2.353 ± 0.014

a = 0.03058 b = 0.01864 f = 0.15

Infinite delta titer 69.2 ml. of 0.02696 N NaOH

Table 19. Runs BN, BO, and BP. Chloroform in the Presence of 0.080 N Added Salts at 34.92°

Point	Added Salt	Time Seconds	Delta Titer ml.	k x 10^4 l.mole^{-1}sec.$^{-1}$
4	NaBr	6,120	7.70	2.017
3	NaBr	14,970	17.81	2.112
2	NaBr	30,540	31.53	2.247
1	NaBr	61,920	48.71	2.211
Initial	NaBr	(Extrapolated)		1.95
9	NaF	6,120	8.95	2.372
8	NaF	14,880	19.62	2.386
7	NaF	29,760	33.12	2.384
6	NaF	59,940	49.28	2.340
Average	NaF			2.371 ± 0.015
13	$NaNO_3$	6,180	9.17	2.410
12	$NaNO_3$	14,730	19.62	2.410
11	$NaNO_3$	29,610	33.00	2.384
10	$NaNO_3$	59,880	49.41	2.366
Average	$NaNO_3$			2.392 ± 0.018

a = 0.03057 b = 0.01872 f = 0.15

Infinite delta titer 69.5 ml. of 0.02696 N NaOH

Table 20. Runs AK, AL, AM. Chloroform in the Presence of 1.50 N $NaClO_4$ and 0.200 N Added Salts at 35°

Point	Added Salt	Time Seconds	Delta Titer ml.	k x 10^4 l.mole^{-1}sec.$^{-1}$
1	NaBr	5,580	1.32	1.306
2	NaBr	10,980	2.46	1.291
3	NaBr	18,720	4.09	1.329
4	NaBr	27,360	5.88	1.399
Initial	NaBr (Extrapolated)			1.259
5	$NaClO_4$	5,400	1.88	2.112
6	$NaClO_4$	10,860	3.53	1.932
7	$NaClO_4$	18,570	5.52	1.909
8	$NaClO_4$	27,180	7.59	1.957
Average	$NaClO_4$			1.978 ± 0.068
9	NaCl	5,190	1.40	1.503
10	NaCl	10,680	2.92	1.593
11	NaCl	18,330	4.49	1.511
12	NaCl	27,000	6.29	1.543
Average	NaCl			1.538 ± 0.031

a = 0.03059 b = 0.01862 f = 0.15

Infinite delta titer 18.1 ml. of 0.09522 N NaOH

Table 21. Runs BQ and BR. Chloroform in the Presence of 0.0580 N Sodium p-Thiocresolate at 34.95°

Point	Time Seconds	Titer to I_2	Titer to Acid	k x 10^4 l.mole^{-1}sec.$^{-1}$
1	6,000	29.22	42.60	2.302
2	11,460	28.75	38.40	2.322
3	19,440	28.80	32.60	2.448
4	25,650	28.70	29.28	2.409
5	56,160	27.85	17.30	2.412
11	66,060	28.80	14.64	2.425
Average				2.386 ± 0.055
6	6,750	29.98	42.00	2.307
7	11,400	29.00	38.38	2.341
9	25,560	28.50	29.30	2.413
10	53,820	28.15	17.88	2.429
12	67,350	28.50	14.60	2.385
Average				2.375 ± 0.039

a = 0.03079 b = 0.02546 f = 0.15 p = 0.1264

Infinite titer to acid = 0.0 ml. of 0.05327 N p-toluene-sulfonic acid

I_2 solution = 0.1989 N.

Table 22. Run M. Chloroform in 67 Per Cent Dioxane at 34.95°

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$ $l.mole^{-1}sec.^{-1}$
1	6,180	4.14	3.178
2	12,060	7.21	3.115
3	18,000	9.95	3.168
4	24,840	12.25	3.104
5	30,240	14.12	3.198
Average			3.153 ± 0.034

a = 0.03049 b = 0.0239 f = 0.15

Infinite delta titer 24.7 ml. of 0.09542 N NaOH

Multiple flask technique

Table 23. Run U. Chloroform in 67 Per Cent Dioxane at 35.0°

Point	Time Seconds	Delta Titer ml.	k x 10^4 l. $mole^{-1}sec.^{-1}$
2	6,090	1.92	3.242
3	11,940	3.40	3.209
4	18,090	4.70	3.201
5	25,290	5.96	3.125
6	29,490	6.55	3.179
Average			3.191 ± 0.031

a = 0.02739 b = 0.02387 f = 0.15

Infinite delta titer 12.5 ml. of 0.03817 N NaOH

Table 24. Run V. Chloroform in 67 Per Cent Dioxane at 35°

Point	Time Seconds	Delta Titer ml.	k x 10^4 l.mole^{-1}sec.$^{-1}$
2	5,880	1.98	3.281
3	12,030	3.66	3.290
4	18,210	4.92	3.187
5	24,810	6.13	3.207
6	28,860	6.73	3.187
7	81,450	10.65	3.006
Average			3.193 ± 0.066

a = 0.02894 b = 0.02390 f = 0.15

Infinite delta titer 12.55 ml. of 0.03817 N NaOH

Table 25. Run AC. Chloroform in Water at 35.0°

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$	$l.mole^{-1} sec.^{-1}$
7	6,030	2.61	2.448	
8	11,910	4.61	2.359	
9	17,520	6.53	2.448	
10	22,320	7.84	2.427	
11	56,700	13.94	2.427	
Average			2.423 ± 0.026	

a = 0.03059 b = 0.01892 f = 0.15

Infinite delta titer 19.87 ml. of 0.09522 N NaOH

Table 26. Run AD. Chloroform in Water at 35.0°

Point	Time Seconds	Delta Titer ml.	k x 10^4 l.mole^{-1}sec.$^{-1}$
2	6,480	2.69	2.363
3	12,270	4.76	2.374
4	17,940	6.56	2.407
5	22,800	7.95	2.431
13	56,940	13.99	2.425
Average			2.392 ± 0.024

a = 0.03059 b = 0.01892 f = 0.15

Infinite delta titer 19.87 ml. of 0.09522 N NaOH

Table 27. Run AE. Chloroform in 40 Per Cent Dioxane at 35.0°

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$ $l.mole^{-1} sec.^{-1}$
2	5,220	2.61	3.216
3	9,195	4.36	3.288
4	13,080	5.78	3.282
5	15,660	6.72	3.342
6	18,780	7.63	3.332
7	23,280	8.84	3.352
Average			3.303 ± 0.041

a = 0.03233 b = 0.02277 f = 0.15

Infinite delta titer 16.85 ml. of 0.02696 N NaOH

Table 28. Run AF. Chloroform in 40 Per Cent Dioxane at 35.0°

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$ $l.mole^{-1}sec.^{-1}$
2	5,070	2.74	3.356
3	9,180	4.48	3.303
4	13,035	5.91	3.243
5	15,705	6.84	3.269
6	18,675	7.85	3.335
7	23,190	9.04	3.328
Average			3.306 ± 0.034

a = 0.03332 b = 0.02299 f = 0.15

Infinite delta titer 17.1 ml. of 0.02696 N NaOH

Table 29. Run AG. Chloroform in 40 Per Cent Dioxane at 35.0°

Point	Time Seconds	Delta Titer ml.	k x 10^4 $l.mole^{-1}sec.^{-1}$
2	4.785	2.65	3.337
3	8,850	4.49	3.331
4	12,780	6.04	3.322
5	15,300	6.89	3.309
6	18,330	7.86	3.325
7	22,860	9.01	3.277
Average			3.317 ± 0.016

a = 0.03437 b = 0.02284 f = 0.15

Infinite delta titer 16.95 ml. of 0.02696 N NaOH

Table 30. Runs AS and AT. Chloroform in Water at 0.0°

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$ $l.mole^{-1}sec.^{-1}$
S-5	326,910	0.53	0.005736
S-6	698,970	1.08	0.005692
S-7	1,203,210	1.75	0.005414
T-3	242,070	0.48	0.007092
T-4	326,220	0.56	0.006082
T-5	697,020	1.22	0.006414
T-6	1,202,520	1.79	0.005520

a = 0.03180 b = 0.03776 f = 0.15

Infinite delta titer 28.0 ml. of 0.02696 N NaOH

Table 31. Runs AY and AZ. Chloroform in Water at 0.0°

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$ $l.mole^{-1}sec.^{-1}$
Y-2	445,950	2.56	0.005412
Y-3	448,560	2.86	0.006095
Y-4	951,840	5.60	0.005797
Z-2	82,230	0.59	0.006844
Z-3	447,240	2.89	0.006157
Z-4	952,020	5.77	0.005997

a = 0.04885 b = 0.09480 f = 0.15

Infinite delta titer 70.3 ml. of 0.02696 N NaOH

Average of Runs AS, AT, AY, and AZ 0.006019 ± 0.000394

Table 32. Run AU. Chloroform in 66-2/3 Per Cent Dioxane at 0.0°

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$ $l.mole^{-1}sec.^{-1}$
2	348,510	0.70	0.011771
3	620,160	1.03	0.009833
4	1,120,500	1.83	0.009968

a = 0.03045 b = 0.02460 f = 0.15

Infinite delta titer 18.2 ml. of 0.02696 N NaOH

Table 33. Run AV. Chloroform in 66-2/3 Per Cent Dioxane at 0.0°

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$ $l.mole^{-1}sec.^{-1}$
3	621,810	1.01	0.009382
4	1,120,050	2.07	0.011099

a = 0.03120 b = 0.02460 f = 0.15

Infinite delta titer 18.2 ml. of 0.02696 N NaOH

Average of Runs AU and AV 0.01041 ± 0.00081

Table 34. Run P. Dichloroiodomethane in 67 Per Cent Dioxane at 34.95°

Point	Time Seconds	Delta Titer ml.	k x 10^4 l.mole^{-1}sec.$^{-1}$
2	528	1.93	39.67
3	1,088	3.66	40.77
4	1,701	5.05	39.91
6	2,838	7.03	39.67
7	3,058	7.37	39.97
8	3,549	7.94	39.48
9	4,087	8.57	40.03
10	4,722	9.06	39.15
11	5,377	9.57	39.28
Average			39.77 ± 0.33

a = 0.02657 b = 0.02337 f = 0.15

Infinite delta titer 12.26 ml. of 0.03817 N NaOH

Table 35. Run S. Dichloroiodomethane in 67 Per Cent Dioxane at 35.0°

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$ $l.mole^{-1}sec.^{-1}$
2	683	2.53	39.41
3	1,241	4.27	41.09
4	1,916	5.67	39.45
5	2,529	6.83	40.02
6	3,059	7.62	40.05
7	3,627	8.32	40.11
8	4,169	8.83	39.63
Average			39.97 ± 0.40

a = 0.02857 b = 0.02305 f = 0.15

Infinite delta titer 12.1 ml. of 0.03817 N NaOH

Table 36. Run W. Dichloroiodomethane in 67 Per Cent Dioxane at 35.0°

Point	Time Seconds	Delta Titer ml.	k x 10^4 l.mole^{-1}sec.$^{-1}$
2	606	2.62	40.56
3	1,203	4.52	40.06
4	1,876	6.10	39.30
5	2,385	7.14	39.90
6	3,015	8.12	39.98
7	3,560	8.83	40.32
8	4,361	9.68	39.57
9	4,777	9.95	40.65
10	5,362	10.32	40.59
Average			40.10 ± 0.38

a = 0.03247 b = 0.02301 f = 0.15

Infinite delta titer 12.08 ml. of 0.03817 N NaOH

Table 37. Run X. Dichloroiodomethane in 40 Per Cent Dioxane at 35.0°

Point	Time Seconds	Delta Titer ml.	k x 10^4 $l.mole^{-1}sec.^{-1}$
2	604	1.31	21.26
3	1,114	2.43	22.84
4	1,796	3.60	22.56
5	2,409	4.51	22.55
6	2,969	5.26	22.58
7	3,612	6.01	22.57
8	4,377	6.73	22.27
9	4,883	7.20	22.40
10	5,628	7.73	22.09
Average			22.35 ± 0.31

a = 0.02874 b = 0.02313 f = 0.15

Infinite delta titer 12.1 ml. of 0.03817 N NaOH

Table 38. Run Y. Dichloroiodomethane in 40 Per Cent Dioxane at 35.0°

Point	Time Seconds	Delta Titer ml.	k x 10^4 l.$mole^{-1}sec.^{-1}$
13	1,246	3.06	22.86
14	1,757	4.08	23.04
15	2,370	5.11	23.01
16	2,987	6.03	23.20
17	3,565	6.65	22.61
18	4,233	7.45	23.04
19	4,802	7.92	22.69
20	5,400	8.53	23.31
Average			22.97 ± 0.19

a = 0.03280 b = 0.02355 f = 0.15

Infinite delta titer 12.35 ml. of 0.03817 N NaOH

Table 39. Run AA. Dichloroiodomethane in 40 Per Cent Dioxane at 35.0°

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$ $l.mole^{-1} sec.^{-1}$
2	575	1.47	22.86
3	1,239	2.93	23.01
4	1,850	4.06	22.94
5	2,485	5.09	23.00
6	3,014	5.80	22.82
8	3,964	7.02	23.32
9	4,815	7.70	22.40
Average			22.91 ± 0.18

a = 0.03033 b = 0.02412 f = 0.15

Infinite delta titer 12.65 ml. of 0.03817 N NaOH

Table 40. Run AO. Dichloroiodomethane in Water at 35.0°

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$ l.mole^{-1}sec.$^{-1}$
2	675	0.19	42.68[c]
3	1,320	0.35	33.78[c]
4	2,568	0.37	14.78
5	3,432	0.42	12.51
6	4,559	0.59	13.68
7	6,488	0.75	12.34
8	9,949	1.17	12.82
9	17,224	1.85	12.19
Average			13.053 ± 0.80

a = 0.002249 b = 0.004697 f = 0.15

Infinite delta titer 13.9 ml. of 0.02696 N NaOH

[c]Not averaged

Table 41. Run AP. Dichloroiodomethane in Water at 35.0°

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$ $l.mole^{-1}sec.^{-1}$
2	7,845	1.05	14.175
3	16,635	2.04	13.650
4	25,860	2.79	12.790
5	64,800	5.28	11.695
6	89,700	6.54	11.764
7	100,650	7.03	11.850
Average			12.654 ± 0.884

a = 0.002276 b = 0.004761 f = 0.15

Infinite delta titer 14.1 ml. of 0.02696 N NaOH

Table 42. Run AW. Dichloroiodomethane in 66-2/3 Per Cent Dioxane at 0.0°

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$ $l.mole^{-1}$ $sec.^{-1}$
2	11,520	0.21	0.1153
3	57,720	1.06	0.1217
4	147,020	2.35	0.1107
5	158,460	2.77	0.1232
6	242,250	3.84	0.1167
7	438,420	6.20	0.1162
8	619,200	7.98	0.1162
9	786,240	9.13	0.1119
10	786,240	9.14	0.1120
11	786,240	9.14	0.1120
Average			0.1156 ± 0.0032

a = 0.02791 b = 0.02418 f = 0.15

Infinite delta titer 17.9 ml. of 0.02696 N NaOH

Table 43. Run AX. Dichloroiodomethane in 66-2/3 Per Cent Dioxane at 0.0°

Point	Time Seconds	Delta Titer ml.	k x 10^4 l.mole^{-1}sec.$^{-1}$
2	55,170	1.01	0.1231
3	57,500	1.02	0.1183
4	145,380	2.51	0.1256
5	157,770	2.80	0.1277
6	242,770	3.95	0.1230
7	440,550	6.46	0.1248
8	618,840	8.05	0.1204
9	787,560	9.21	0.1160
10	787,560	9.18	0.1152
11	787,560	9.29	0.1174
Average			0.1207 ± 0.00369

a = 0.02730 b = 0.02419 f = 0.15

Infinite delta titer 17.9 ml. of 0.02696 N NaOH

Table 44. Run AI. Bromochlorofluoromethane in 66-2/3 Per Cent Dioxane at 0.0°

Point	Time Seconds	Delta Titer ml.	k x 10^4 l.mole^{-1}sec.$^{-1}$
2	106	0.81	178.7[c]
3	329	2.22	173.3[c]
4	514	3.51	192.3
5	932	5.44	193.4
6	1,573	7.42	190.2
7	2,623	9.23	184.0
8	2,954	9.67	185.0
Average			188.9 ± 3.7

a = 0.009882 b = 0.01676 f = 0.653

Infinite delta titer 12.40 ml. of 0.02696 N NaOH

[c]Not averaged

Table 45. Run AJ. Bromochlorofluoromethane in 66-2/3 Per Cent Dioxane at 0.0

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$ $l.mole^{-1}sec.^{-1}$
2	110	0.85	226.4
3	338	2.11	197.6
4	568	3.12	188.9
5	921	4.46	184.7
6	1,604	6.61	196.5
7	2,604	8.43	195.1
8	3,003	8.95	194.7
Average			191.98 ± 4.14

a = 0.007925 b = 0.01713 f = 0.605

Infinite delta titer 12.70 ml. of 0.02696 N NaOH

Table 46. Run AN. Bromochlorofluoromethane in Water at 0.0°

Point	a	Time Seconds	Delta Titer ml.	$k \times 10^4$ $l.mole^{-1}sec.^{-1}$
3	0.06423	539	6.77	18.10
2	0.06385	1,453	13.49	15.58
4	0.06394	1,764	15.07	14.88
5	0.06363	2,577	18.88	14.29
6	0.06349	4,087	23.91	13.68
Average				15.31 ± 1.21

b = 0.018068 f = 0.629

Infinite delta titer 33.45 ml. of 0.02696 N NaOH

Table 47. Run AQ. Bromochlorofluoromethane in 40 Per Cent Dioxane at 0.0°

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$ l.mole^{-1} sec.$^{-1}$
2	448	1.99	95.29
3	938	3.77	117.3[c]
4	1,393	4.88	90.78
5	1,900	6.07	90.31
6	2,443	7.09	89.33
7	3,525	8.60	86.20
Average			90.38 ± 2.12

a = 0.009119 b = 0.02115 f = 0.629

Infinite delta titer 15.65 ml. of 0.02696 N NaOH

[c]Not averaged

Table 48. Run AR. Bromochlorofluoromethane in 40 Per Cent Dioxane at 0.0°

Point	Time Seconds	Delta Titer ml.	k x 10^4 $l.mole^{-1}sec.^{-1}$
2	486	1.91	90.64
3	1,024	3.53	88.59
4	1,446	4.53	85.96
5	2,054	5.88	86.97
6	2,506	6.63	85.40
7	3,836	8.34	82.01[c]
Average			87.51 ± 1.68

a = 0.008431 b = 0.02129 f = 0.629

Infinite delta titer 15.8 ml. of 0.02696 N NaOH

[c]Not averaged

Table 49. Runs BB and BG. Bromochlorofluoromethane in 66-2/3 Per Cent Dioxane at 14.3°

Point	Time Seconds	Delta Titer ml.	k x 10^4 $l.mole^{-1}sec.^{-1}$
B-2	257	6.57	2,275
B-3	480	7.99	2,058
B-4	690	8.71	2,012
B-5	892	9.65	2,050
Average			2,099 ± 88
G-2	192	5.68	2,260
G-3	422	7.92	2,277
G-4	622	8.64	2,153
G-5	845	9.09	2,083
Average			2,193 ± 75

a = 0.006868 b = 0.01308 f = 0.625

Infinite delta titer 9.7 ml. of 0.02696 N NaOH

Table 50. Run BC. Dibromochloromethane in 66-2/3 Dioxane at 0.0°

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$ $l.mole^{-1}sec.^{-1}$
2	99,150	4.07	0.1274[c]
3	107,520	4.69	0.1385
4	160,050	6.59	0.1395
5	268,800	9.37	0.1340
Average			0.1375 ± 0.0023

a = 0.05787 b = 0.03694 f = 0.083

Infinite delta titer 20.53 ml. of 0.02696 N NaOH

[c]Not averaged

Table 51. Run BD. Dibromochloromethane in 66-2/3 Per Cent Dioxane at 0.0°

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$ $l.mole^{-1}sec.^{-1}$
2	99,570	4.24	0.1327
3	107,400	4.77	0.1407
4	160,350	6.64	0.1411
5	268,620	9.41	0.1344
Average			0.1372 ± 0.0037

a = 0.05787 b = 0.03703 f = 0.083

Infinite delta titer 20.55 ml. of 0.02696 N NaOH

Table 52. Runs EE and EF. Dichlorobromomethane in 66-2/3 Per Cent Dioxane at 0.0°

Point	Time Seconds	Delta Titer ml.	$k \times 10^4$ $l.mole^{-1}sec.^{-1}$
E-2	99,420	9.25	0.3344
E-3	106,620	10.21	0.3604
E-4	159,630	12.97	0.3563
Average			0.3504 ± 0.0106
F-2	101,160	9.46	0.3404
F-3	106,740	10.04	0.3522
F-4	159,870	13.14	0.3669
Average			0.3532 ± 0.0092

a = 0.06004 b = 0.03694 f = 0.15

Infinite delta titer 20.53 ml. of 0.02696 N NaOH

Table 53. Run BS. Fluoroform in Water at 50°

Point	Time Seconds	Base Titer ml.
1	0	0.44
2	77,730	0.45
3	270,870	0.40
4	2,148,170	0.13

Procedure: Approximately 250 ml. of boiled distilled water was saturated with fluoroform at 5° and 740 mm. pressure. Two hundred milliliters of this solution, measured at 35°, was placed in a round bottom flask in the water bath at 50°. The reaction was started by the addition of 50 ml. of 0.1776 N NaOH. Fifteen milliliter samples were withdrawn into flasks containing 5.00 ml. of 0.1112 N p-toluenesulfonic acid. The excess acid was back-titrated with 0.09542 N NaOH.

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VITA

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Arthur Maultsby Dowell, Jr. was born on August 14, 1922, at Birmingham, Alabama. He is the son of Alma (nee Papot) and Arthur M. Dowell. After attending the public schools in Birmingham, he graduated from Erskine Ramsay High School there in January, 1939. After one year at Birmingham-Southern College, he entered Howard College and graduated in June, 1943, with a Bachelor of Science degree in Chemistry. In July of 1943, he began graduate work in chemistry at the Georgia School of Technology. He married Flonnie Turner Cooper in August of that year. In March, 1944, he left Georgia Tech and in May entered the U. S. Navy. After serving in the fleet as a Radio Technician, Second Class, he was discharged in February of 1946 and accepted a position as instructor in the Chemistry Department of the Georgia School of Technology until the fall, at which time he resumed work on his Master of Science degree at the same school. After receiving this degree in June, 1947, and serving one year as instructor in chemistry at the Georgia Institute of Technology, the next three years were spent as Assistant Professor of Chemistry at Hampden-Sydney College, Virginia. He returned to the Georgia Institute of Technology during the summer of 1951 to resume graduate study. He held a National Science Foundation Fellowship for the year 1952-53, and a Graduate Division Fellowship for the Spring Quarter of 1953. He is now employed as a Research Chemist with the Cellulose and Specialties Division of the Buckeye Cotton Oil Company in Memphis, Tennesee.

He is the father of three children, Arthur M. III, Flonnie, and Paul C. Dowell.